



Short Communication

Stability of thin emulsion film between two oil phases with a viscoelastic liquid–liquid interface

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ABSTRACT

The viscoelastic properties of adsorbed protein layer in food emulsions and foams are important in providing stability to such systems. Linear stability analysis for a protein stabilized aqueous film sandwiched between two semi-infinite oil phases with a viscoelastic liquid–liquid interface is presented. The interfacial dilatational and shear viscoelastic properties are described by Maxwell models. The aqueous film is found to be more stable for smaller values of dilatational (shear) relaxation times and larger values of interfacial dilatational (shear) viscosities. The asymptotic values of maximum growth coefficient for very large and very small values of interfacial dilatational (shear) viscosities were found to be independent of relaxation times and correspond to those for immobile and fully mobile liquid–liquid interfaces respectively. The aqueous film is shown to be more stable for larger viscosities of the oil phase with the maximum growth coefficient approaching zero as the ratio of viscosities of oil and aqueous phases approach very large values and an asymptotic value corresponding to that for a foam film for very small viscosity ratios.

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1. Introduction

Thin liquid films are encountered in many food colloidal systems such as foams, emulsions, dispersions etc. Some of the examples of such food systems are whipped toppings, salad dressing, mayonnaise, ice cream etc. The stability of such systems depends on the stability of thin film separating gas bubbles, emulsion droplets and dispersed particles. Food emulsifiers and proteins are usually employed to provide stability to such colloidal systems. In foams and emulsions, liquid from thin films drains due to capillary forces as a result of surface/interfacial tension and radius of curvature of film interface. The capillary pressure, responsible for film drainage, is counterbalanced by intermolecular van der Waals, steric, electrostatic, hydration and depletion interactions whenever the film thickness becomes of the order of a few nanometers so that the film eventually reaches a mechanical equilibrium. These intermolecular interactions are mainly influenced by the emulsifiers and proteins that are employed in such systems. Interfacial tension and repulsive interactions between the two faces of the film will tend to attenuate any imposed perturbations whereas the van der Waals interactions will tend to enhance them thereby re-

sulting in their growth. The film is deemed stable if the imposed perturbations decay whereas the growth of the perturbations will lead to eventual film rupture. Extensive investigations [1–9] on linear stability analysis of equilibrium thin films have been carried out to evaluate the growth of perturbations and the timescale of resulting film rupture. Recent studies have extended the analysis of rupture of thin film on solid [10,11] as well as foam film [12] due to imposed random mechanical perturbations. The effect of these intermolecular interactions is usually accounted for through a disjoining pressure [13] in the normal stress boundary conditions. It has been shown that the imposed perturbations grow whenever this disjoining pressure gradient (with respect to film thickness) is positive [3]. The rupture time of an equilibrium film can be evaluated as the time at which the amplitude of growing imposed perturbation equals one half the film thickness. Previous studies have investigated the effects of density variations [14] and hydrophobic interactions [15] on film stability. Rupture of non-Newtonian [16,17] as well as viscoelastic [18,19] thin films have been investigated. The analysis has been extended to rupture of a draining film due to imposed thermal [13,20] as well as random mechanical [21] perturbations. In food systems, proteins are extensively employed to provide stability to emulsions and foams by modifying the interparticle forces and, more importantly, by providing improved interfacial rheological properties to the oil–water and air–water interfaces. Surface rheological measurements have

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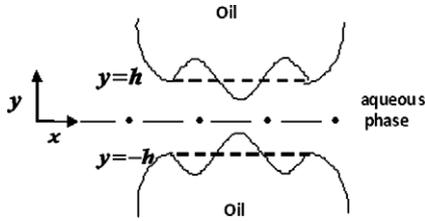


Fig. 1. Schematic of a thin emulsion film between two semi-infinite oil phases.

shown that adsorbed films of disordered proteins (such as α_1 -casein, β -casein) have a low surface shear viscosity whereas films of globular proteins (such as α -lactalbumin, β -lactoglobulin) are highly viscous [22–25]. The viscoelastic properties of adsorbed protein film are important for stabilizing oil droplet and gas bubbles against coalescence in emulsion and foam systems [26,27]. In a previous study [28], we have investigated the stability of a thin film on a solid surface with a viscoelastic air–liquid interface by linear stability analysis. In this study, we extend this analysis to an aqueous thin film sandwiched between two semi-infinite oil phases accounting for the viscoelastic nature of oil–water interface. The stability analysis gives information on the dependence of maximum growth coefficient and film rupture time on interfacial viscoelastic properties.

2. Governing equations

Consider a thin protein stabilized aqueous film of thickness $2h$ sandwiched between two semi-infinite oil phases. The schematic of the film is shown in Fig. 1. The film is of length L in the x direction and can be considered semi infinite in the other direction. The plane of symmetry is the origin of y direction. Therefore, $y = \pm h$ refer to the top and bottom oil–water interfaces respectively. At $t = 0$, an asymmetric periodic perturbation $f_0 \sin(kx)$ of wavenumber k is imposed on the two faces of the film. The imposition of this perturbation will result in a flow within the film which is also influenced by Marangoni flow. If the perturbation grows, the film will eventually rupture; otherwise the film will be stable. The equations to describe the flow due to imposed disturbance are given by.

2.1. Aqueous film

The continuity equation is

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0. \quad (1)$$

Assuming quasi-steady state, the equations of motion are

$$-\frac{\partial p}{\partial x} + \mu \left(\frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} \right) = 0, \quad (2)$$

$$-\frac{\partial p}{\partial y} + \mu \left(\frac{\partial^2 v_y}{\partial x^2} + \frac{\partial^2 v_y}{\partial y^2} \right) = 0. \quad (3)$$

The validity of the assumption of quasi-steady state is discussed elsewhere [11]. Since the motion in the liquid film is due to the imposed perturbation, it is reasonable to assume that the film thickness $h(x, t)$, pressure $p(x, y, t)$, velocity in x direction $v_x(x, y, t)$, and velocity in y direction $v_y(x, y, t)$ also have oscillations of the same frequency as the imposed perturbation, i.e.,

$$f(x, t) = f_0 \exp(ikx + \beta t), \quad (4)$$

$$p(x, y, t) = p_{ss} + p'(y) \exp(ikx + \beta t), \quad (5)$$

$$v_x(x, y, t) = v'_x(y) \exp(ikx + \beta t), \quad (6)$$

$$v_y(x, y, t) = v'_y(y) \exp(ikx + \beta t), \quad (7)$$

where p_{ss} is the pressure in the Plateau border and β is the growth coefficient. If β is positive, then the amplitude of perturbation will keep increasing resulting in rupture of the film, otherwise the perturbation decreases and disappears eventually.

Symmetry condition at the midpoint gives,

$$y = 0, \quad \frac{\partial v_x(x, 0, t)}{\partial y} = 0, \quad (8)$$

$$y = 0, \quad \frac{\partial v_y(x, 0, t)}{\partial y} = 0. \quad (9)$$

At the oil–water interface, the kinematic condition gives,

$$y = h, \quad v_y(x, h, t) = \frac{\partial f}{\partial t}. \quad (10)$$

It is to be noted that the surfactant (protein) is soluble only in the aqueous phase. Equation of continuity for the surfactant in the aqueous phase for quasi steady state yields,

$$\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} = 0 \quad (11)$$

with the boundary conditions,

$$x = 0, \quad c = c_0,$$

$$x = L, \quad c = c_0, \quad (12)$$

$$y = 0, \quad \frac{\partial c}{\partial y} = 0. \quad (13)$$

The surfactant flux to the interface can be decomposed into (i) diffusive flux j_{diff} to the subsurface and (ii) adsorptive flux j_{ads} from the subsurface to the interface. These are given by,

$$j_{diff} = -D \frac{\partial c}{\partial y} \quad \text{at } y = y_{sub}, \quad (14)$$

where y_{sub} refers to the location of the subsurface and

$$j_{ads} = -k_{ads}(\Gamma - \Gamma_0(c_{sub})). \quad (15)$$

In the above equation, k_{ads} is the adsorption rate constant, Γ is the surface concentration of surfactant and $\Gamma_0(c_{sub})$ is the equilibrium surface concentration corresponding to the subsurface concentration c_{sub} . The above equation is written for small deviation from the equilibrium [13]. When the energy barrier to adsorption is small (much less than kT), every surfactant molecule is immediately adsorbed upon its arrival at the subsurface. In this case, the surfactant transport to the interface is governed by Eq. (14) [13]. Also, for small subsurface thickness, $y_{sub} \approx h$.

Surfactant balance at the liquid–liquid interface yields,

$$-D \frac{\partial c}{\partial y} \Big|_{y=h} = \frac{\partial}{\partial x} (\Gamma v_x^0) - D_s \frac{\partial^2 \Gamma}{\partial x^2} + \frac{\partial \Gamma}{\partial t}, \quad (16)$$

where D and Γ are the diffusion coefficient and surface concentration of surfactant respectively in the aqueous phase, v_x^0 is the interfacial velocity of the film and D_s is the surface diffusion coefficient. It is to be noted that the surfactant is not soluble in the oil phase. Therefore, oil phase need not be included in the above conservation equation for the surfactant, Eq. (16) can be rewritten as,

$$-D \frac{\partial c}{\partial y} \Big|_{y=h} = \frac{\partial}{\partial x} (\Gamma v_x^0) - D_s \frac{\partial^2 \Gamma}{\partial x^2} + \left(\frac{\partial \Gamma}{\partial c} \right) \frac{\partial c}{\partial t}. \quad (17)$$

For Langmuir adsorption isotherm,

$$\Gamma_0 = \frac{\Gamma_m Kc}{1 + Kc}, \quad (18)$$

where K and Γ_m are constants. Equation (17) can be non-dimensionalized to yield,

$$-\frac{\partial c^*}{\partial y^*} \Big|_{y^*=1} = \left(\frac{\Gamma_0 V h}{D c_0 L} \right) \frac{\partial \Gamma^* v_x^{0*}}{\partial x^*} - \frac{D_s \left(\frac{\partial \Gamma}{\partial c} \right) h}{DL^2} \frac{\partial^2 c^*}{\partial x^{*2}} + \frac{\left(\frac{\partial \Gamma}{\partial c} \right) h}{D \tau} \frac{\partial c^*}{\partial t^*} \tag{19a}$$

In the last term, $\frac{(\partial \Gamma / \partial c) h}{D \tau}$ is a modified Peclet number whose value will depend on the adsorption isotherm and surfactant concentration. The temporal variation of surface concentration can be neglected if $\frac{(\partial \Gamma / \partial c) h}{D \tau} \ll 1$. In addition, $\Gamma = \Gamma_0 + \Gamma_1$, where Γ_0 is the equilibrium surface concentration and Γ_1 is the deviation from the equilibrium due to interfacial mobility. We assume that $\Gamma_1 \ll \Gamma_0$ [11,13,29] so that Eq. (19a) can be approximated as,

$$-\frac{\partial c^*}{\partial y^*} \Big|_{y^*=1} = \left(\frac{\Gamma_0 V h}{D c_0 L} \right) \frac{\partial v_x^{0*}}{\partial x^*} - \frac{D_s \left(\frac{\partial \Gamma}{\partial c} \right) h}{DL^2} \frac{\partial^2 c^*}{\partial x^{*2}} \tag{19b}$$

For typical values $K = 6$; $\Gamma_m = 5 \times 10^{-8}$ moles/m², $\left(\frac{\Gamma_0 V h}{D c_0 L} \right) = 2.6 \times 10^{-12}$ and $\frac{D_s \left(\frac{\partial \Gamma}{\partial c} \right) h}{DL^2} = 2.5 \times 10^{-14}$. Therefore, surface diffusion term is much smaller than the convection term in Eq. (19b) which can then be approximated as

$$-D \frac{\partial c}{\partial y} \Big|_{y=h} = \Gamma_0 \frac{\partial}{\partial x} (v_x^0) \tag{20}$$

Assuming the surfactant concentration profile in the aqueous phase is of the form,

$$c'(x, y) = \frac{c(x, y) - c_0}{c_0} = C \exp(ikx) \cosh(ky) \tag{21}$$

Equation (11) can be solved with the boundary conditions (12) and (13) to yield,

$$\frac{\partial c}{\partial x} = \frac{\Gamma_0 v_x'(h) k^2}{Dk \sinh kh} \cosh ky \exp(ikx + \beta t) \tag{22}$$

Using Gibbs adsorption equation,

$$\Gamma_0 = -RTc \frac{d\sigma}{dc} \tag{23}$$

where R is gas constant, T is temperature and σ is the interfacial tension.

2.2. Oil phase

In order to solve the normal and shear stress balance at the oil–water interface, we need to solve for the velocity field in the oil phase. The equations of continuity and motion in the oil phase are given by

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} = 0, \tag{24}$$

where u_x and u_y refer to the x and y components of velocity respectively in the oil phase.

$$-\frac{\partial p_d}{\partial x} + \mu_d \left(\frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2} \right) = 0, \tag{25}$$

$$-\frac{\partial p_d}{\partial y} + \mu_d \left(\frac{\partial^2 u_y}{\partial x^2} + \frac{\partial^2 u_y}{\partial y^2} \right) = 0, \tag{26}$$

where p_d is the pressure and μ_d is the viscosity of oil phase respectively. It is reasonable to assume

$$p_d(x, y, t) = p_{d,ss} + p'_d(y) \exp(ikx + \beta t), \tag{27}$$

$$u_x(x, y, t) = u'_x(y) \exp(ikx + \beta t), \tag{28}$$

$$u_y(x, y, t) = u'_y(y) \exp(ikx + \beta t), \tag{29}$$

where $p_{d,ss}$ is the bulk pressure in the oil phase (far from the interface). The velocity fields in the aqueous and oil phases should satisfy the following boundary conditions:

Continuity at the interface:

$$y = h, \quad u_x(x, y, t) = v_x(x, y, t), \tag{30}$$

$$y = h, \quad u_y(x, y, t) = v_y(x, y, t), \tag{31}$$

$$y \rightarrow \infty, \quad u_x(x, y, t) = 0, \tag{32}$$

$$y \rightarrow \infty, \quad u_y(x, y, t) = 0. \tag{33}$$

At the oil–water interface, normal force balance results in normal stress boundary conditions as given by [28,30]

$$-\underline{\underline{n}} P \underline{\underline{n}} \underline{\underline{n}} = 2H\sigma \underline{\underline{n}} + \int_{-\infty}^t G_s(t-t') \underline{\underline{n}} (\underline{\underline{b}} - 2H \underline{\underline{I}}_s) : \nabla_s \underline{\underline{v}}^0 dt' + \int_{-\infty}^t G_d(t-t') 2H \underline{\underline{n}} \nabla_s \cdot \underline{\underline{v}}^0 dt' + \int_{-\infty}^t G_s(t-t') 2H \underline{\underline{n}} \nabla_s \cdot \underline{\underline{v}}^0 dt' \tag{34}$$

where $\underline{\underline{P}}$ refers to the difference in the pressure tensor across the interface, $G_s(t)$ and $G_d(t)$ refer to the surface shear and surface dilatational relaxation modulus respectively, H is the curvature of the interface, σ is the surface tension, $\underline{\underline{n}}$ is the unit normal, $\underline{\underline{v}}^0$ is the surface velocity vector, $\underline{\underline{b}}$ is the surface curvature dyadic defined as, $\underline{\underline{b}} = -\nabla_s \cdot \underline{\underline{n}}$, ∇_s being the surface gradient operator. Since $\underline{\underline{I}}_s : \nabla_s \underline{\underline{v}}^0 = \nabla_s \cdot \underline{\underline{v}}^0$, we have,

$$-\underline{\underline{n}} P \underline{\underline{n}} \underline{\underline{n}} = 2H\sigma \underline{\underline{n}} + \int_{-\infty}^t G_s(t-t') \underline{\underline{n}} \underline{\underline{b}} : \nabla_s \underline{\underline{v}}^0 dt' + \int_{-\infty}^t G_d(t-t') 2H \underline{\underline{n}} \nabla_s \cdot \underline{\underline{v}}^0 dt' \tag{35}$$

For a planar liquid–liquid interface, the above normal stress boundary condition becomes,

$$p(x, h, t) - p_d(x, h, t) + \Pi(h) + 2\Pi'(h)f - 2\mu \frac{\partial v_y}{\partial y} + 2\mu_d \frac{\partial u_y}{\partial y} = h_1 \frac{\partial}{\partial y} \left(\frac{1}{h_1} \right) \left[\sigma + \left\{ \int_{-\infty}^t G_d(t-t') + G_s(t-t') \right\} \times \left\{ h_1 \frac{\partial}{\partial x} v_x^0 + v_y^0 h_1 \frac{\partial}{\partial y} \left(\frac{1}{h_1} \right) \right\} dt' \right], \tag{36}$$

where $p(x, t)$ is the pressure inside the film, $p_d(x, h, t)$ is the pressure in the oil phase, $\Pi(h)$ is the van der Waals disjoining pressure given by

$$\Pi(h) = -\frac{A_{eff}}{24\pi h^3}, \tag{37}$$

where A_{eff} is the effective Hamaker constant. The contribution of electrostatic interaction to the disjoining pressure may not be important at sufficiently high ionic strengths because of compression of electrical double layer. In addition, the contribution of steric interaction, being short range compared to van der Waals interaction, is not considered here. In Eq. (36), $\Pi'(h)$ is the gradient of the disjoining pressure with respect to film thickness, μ and μ_d are the bulk viscosity of the aqueous and oil phases respectively, σ is the

interfacial tension and h_1 is the surface metric (the other metric h_2 being unity). Recognizing that

$$h_1 = \frac{dl}{dx} = \sqrt{1 + \left(\frac{df}{dx}\right)^2}$$

we get,

$$p(x, h, t) - p_d(x, h, t) + \Pi(h) + 2\Pi'(h)f - 2\mu \frac{\partial v_y}{\partial y} + 2\mu_d \frac{\partial u_y}{\partial y} = -\frac{\left(\frac{d^2f}{dx^2}\right)}{1 + \left(\frac{df}{dx}\right)^2} \left[\sigma + \int_{-\infty}^t \{G_d(t-t') + G_s(t-t')\} \times \left\{ \sqrt{1 + \left(\frac{df}{dx}\right)^2} \frac{\partial v_x^0}{\partial x} - \frac{v_y^0 \left(\frac{d^2f}{dx^2}\right)}{1 + \left(\frac{df}{dx}\right)^2} \right\} dt' \right]. \tag{38}$$

Retaining only linear terms, we get,

$$p(x, h, t) - p_d(x, h, t) + \Pi(h) + 2\Pi'(h)f - 2\mu \frac{\partial v_y}{\partial y} + 2\mu_d \frac{\partial u_y}{\partial y} = -\sigma \left(\frac{\partial^2 f}{\partial x^2}\right) \tag{39}$$

or,

$$p_{ss} + p'(h) \exp(ikx + \beta t) - p_{d,ss} - p'_d(h) \exp(ikx + \beta t) + \Pi(h) + 2\Pi'(h)f - 2\mu \frac{\partial v_y}{\partial y} + 2\mu_d \frac{\partial u_y}{\partial y} = -\sigma \left(\frac{\partial^2 f}{\partial x^2}\right). \tag{40}$$

Since $p_{ss} - p_{d,ss} + \Pi(h) = 0$ for an equilibrium film, we have,

$$p'(h) \exp(ikx + \beta t) - p'_d(h) \exp(ikx + \beta t) + 2\Pi'(h)f - 2\mu \left(\frac{\partial v_y(h)}{\partial y}\right) + 2\mu_d \left(\frac{\partial u_y(h)}{\partial y}\right) = -\sigma \left(\frac{\partial^2 f}{\partial x^2}\right). \tag{41}$$

From Eqs. (4), (5), (7) and (29), Eq. (41) reduces to

$$p'(h) - p'_d(h) + 2\Pi'(h)f_0 - 2\mu \left(\frac{dv'_y(h)}{dy}\right) + 2\mu_d \left(\frac{du'_y(h)}{dy}\right) = \sigma f_0 k^2. \tag{42}$$

For a viscoelastic interface, shear stress balance can be expressed as [28,30]

$$-\underline{\underline{n}} \parallel \underline{\underline{P}} \parallel \underline{\underline{s}} = \nabla_s \sigma + \int_{-\infty}^t G_d(t-t') \nabla_s \nabla_s \cdot \underline{\underline{v}}^0 dt' + \int_{-\infty}^t G_s(t-t') \nabla_s \nabla_s \cdot \underline{\underline{v}}^0 dt' + \int_{-\infty}^t G_s(t-t') [\underline{\underline{n}} \times \nabla_s [(\nabla_s \times \underline{\underline{v}}^0) \cdot \underline{\underline{n}}]] + 2(\underline{\underline{b}} - 2H\underline{\underline{s}}) \cdot (\nabla_s \underline{\underline{v}}^0) \cdot \underline{\underline{n}} dt'. \tag{43}$$

For a planar liquid–liquid interface, the above shear stress boundary condition becomes,

$$\mu \left(\frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y}\right)_{y=h} - \mu_d \left(\frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y}\right)_{y=h} = h_1 \frac{\partial \sigma}{\partial x} + \int_{-\infty}^t \{G_d(t-t') + G_s(t-t')\} \times \left[h_1 \frac{\partial}{\partial x} h_1 \frac{\partial v_x^0}{\partial x} + h_1 \frac{\partial}{\partial x} v_y^0 \frac{\partial}{\partial y} \left(\frac{1}{h_1}\right) \right] dt', \tag{44}$$

which can be simplified to

$$\mu \left(\frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y}\right)_{y=h} - \mu_d \left(\frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y}\right)_{y=h} = \sqrt{1 + f'^2} \frac{\partial \sigma}{\partial x} + \int_{-\infty}^t \{G_d(t-t') + G_s(t-t')\} \times \left[(1 + f'^2) \frac{\partial^2 v_x^0}{\partial x^2} + \sqrt{1 + f'^2} \frac{\partial v_x^0}{\partial x} \frac{f' f''}{\sqrt{1 + f'^2}} - \sqrt{1 + f'^2} \frac{\partial v_y^0}{\partial x} \frac{f''}{1 + f'^2} - \sqrt{1 + f'^2} v_y^0 \left[\frac{f'''}{1 + f'^2} - \frac{4f''^2 f'}{(1 + f'^2)^2} \right] \right] dt'. \tag{45}$$

Retaining only the linear terms, the above equation reduces to,

$$\mu \left(\frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y}\right)_{y=h} - \mu_d \left(\frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y}\right)_{y=h} = \frac{\partial \sigma}{\partial x} + \int_{-\infty}^t (G_d(t-t') + G_s(t-t')) \frac{\partial^2 v_x^0}{\partial x^2} dt', \tag{46}$$

where v_x^0 is the velocity at the oil–water interface. The first and the second terms on the left-hand side refer to the shear stress due to motion in the aqueous and oil phases respectively. The first term on the right-hand side in Eq. (46) is the Marangoni effect. Equation (46) can be rewritten as,

$$\mu \left(\frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y}\right)_{y=h} - \mu_d \left(\frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y}\right)_{y=h} = \frac{\partial \sigma}{\partial c} \frac{\partial c}{\partial x} + \int_{-\infty}^t (G_d(t-t') + G_s(t-t')) \frac{\partial^2 v_x^0}{\partial x^2} dt'. \tag{47}$$

Using Eqs. (21)–(23), Eq. (47) can be recast as,

$$\mu \left(\frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y}\right)_{y=h} - \mu_d \left(\frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y}\right)_{y=h} = \frac{\partial \sigma}{\partial c} \frac{\Gamma_0 v'_x(h) k^2}{Dk \sinh kh} \cosh ky \exp(ikx + \beta t) + \int_{-\infty}^t (G_d(t-t') + G_s(t-t')) \frac{\partial^2 v_x^0}{\partial x^2} dt'. \tag{48}$$

For a Maxwell model,

$$G_d(s) = \frac{\kappa}{\lambda_d} \exp\left(-\frac{s}{\lambda_d}\right), \tag{49a}$$

$$G_s(s) = \frac{\mu_s}{\lambda_s} \exp\left(-\frac{s}{\lambda_s}\right), \tag{49b}$$

where κ and μ_s are dilatational and shear viscosities respectively. λ_d and λ_s are relaxation times defined as

$$\lambda_d = \frac{\kappa}{g_d}, \tag{50a}$$

$$\lambda_s = \frac{\mu_s}{g_s}, \tag{50b}$$

where g_d and g_s are dilatational and shear elasticity respectively. The solution of equation of continuity and motion for the aqueous thin film give the following solutions for the velocity and pressure,

$$v'_x(y) = i[c_1 \exp(ky) - c_2 \exp(-ky) + c_3 y \exp(-ky)] + \frac{i}{k}[c_3 \exp(ky) + c_4 \exp(-ky)], \quad (51)$$

$$v'_y(y) = c_1 \exp(ky) + c_2 \exp(-ky) + c_3 y \exp(ky) + c_4 y \exp(-ky), \quad (52)$$

$$p'(y) = 2\mu[c_3 \exp(ky) + c_4 \exp(-ky)], \quad (53)$$

and the symmetry conditions (8)–(9) give,

$$c_3 = c_4; \quad c_1 = -\frac{c_3}{k}; \quad c_2 = \frac{c_3}{k}. \quad (54)$$

Similarly, the solution of the equations of continuity and motion for the oil phase with the boundary conditions give the following expressions for the velocity and pressure,

$$u'_y(y) = d_2 \exp(-ky) + d_4 y \exp(-ky), \quad (55)$$

$$u'_x(y) = -i[d_2 \exp(-ky) + d_4 y \exp(-ky)] + \frac{i}{k}d_4 \exp(-ky), \quad (56)$$

$$p'_d(y) = 2\mu_d d_4 \exp(-ky). \quad (57)$$

Substituting the above expressions in the normal stress boundary condition (37), we get,

$$4\mu c_3 \cosh(kh) - 2\mu_d d_4 \exp(-kh) + 2\Pi'(2h)f_0 + 4\mu c_1 k \cosh(kh) + 4\mu c_3 kh \sinh(kh) + 4\mu c_3 \cosh(kh) - 2\mu_d d_2 k \exp(-kh) - 2\mu_d d_4 (1 + kh) \exp(-kh) = \sigma f_0 k^2. \quad (58)$$

Substituting Eqs. (51)–(57) in the shear stress boundary condition (48) gives,

$$\begin{aligned} & \mu k [2c_1 \sinh(kh) + 2c_3 h \cosh(kh)] \\ & + \mu [2c_1 k \sinh(kh) + 4c_3 \sinh(kh) + 2c_3 kh \sinh(kh)] \\ & - 2\mu_d k (d_2 \exp(-kh) + d_4 h \exp(-kh)) - 2\mu_d d_4 \exp(-kh) \\ & = \left[\frac{\partial \sigma}{\partial c} \frac{\Gamma_0 k^2 \cosh(kh)}{Dk \sinh(kh)} - k^2 \left\{ \frac{\kappa}{1 + \beta \lambda_d} + \frac{\mu_s}{1 + \beta \lambda_s} \right\} \right] \\ & \times \left[2c_1 \cosh(kh) + 2c_3 h \sinh(kh) + \frac{2c_3}{k} \cosh(kh) \right]. \quad (59) \end{aligned}$$

The continuity of velocity at the interface yields,

$$2c_1 \sinh(kh) + 2c_3 h \cosh(kh) = d_2 \exp(-kh) + d_1 h \exp(-kh), \quad (60)$$

$$2c_1 \cosh(kh) + 2c_3 h \sinh(kh) + \frac{2}{k} c_3 \cosh(kh) = -d_2 \exp(-kh) - d_4 h \exp(-kh) + \frac{1}{k} d_4 \exp(-kh). \quad (61)$$

Equations (58)–(61) are solved for the constants c_1 , c_3 , d_2 and d_4 and the growth coefficient is calculated from the equation,

$$\beta = \frac{1}{f_0} (2c_1 \sinh(kh) + 2c_3 h \cosh(kh)). \quad (62)$$

Define the following dimensionless parameters,

$$c_1^* = \frac{\mu c_1}{2|\Pi'|h f_0}; \quad c_3^* = \frac{\mu c_3}{2|\Pi'|h}; \quad d_2^* = \frac{\mu d_2}{2|\Pi'|h f_0}; \quad d_4^* = \frac{\mu d_4}{2|\Pi'|h}, \quad (63)$$

$$\mu^* = \frac{\mu_d}{\mu}; \quad cp^* = \frac{\sigma}{2|\Pi'|h^2} = \frac{\pi \sigma h^2}{A_{\text{eff}}}; \quad s^* = \left(\frac{\partial \sigma}{\partial c} \right) \frac{\Gamma_0}{\mu D}, \quad (64)$$

$$\kappa^* = \frac{\kappa}{\mu h}; \quad \mu_s^* = \frac{\mu_s}{\mu h}; \quad k^* = kh, \quad (65)$$

$$\tau = \frac{\mu}{2|\Pi'|h}; \quad \lambda_d^* = \frac{\lambda_d}{\tau}; \quad \lambda_s^* = \frac{\lambda_s}{\tau}; \quad \beta^* = \beta \tau, \quad (66)$$

where τ is the characteristic time, cp^* is the ratio of capillary force and disjoining pressure, k^* is the dimensionless wavenumber, β^* is the dimensionless growth coefficient, κ^* and μ_s^* are the dimensionless surface dilatational and surface viscosity respectively and λ_s^* and λ_d^* refer to dimensionless shear and dilatational relaxation times respectively. The above equations can be recast in terms of these dimensionless variables as,

$$8c_3^* \cosh k^* - 2\mu^* d_4^* \exp(-k^*) + 4c_1^* k^* \cosh k^* + 4c_3^* k^* \sinh k^* - 2\mu^* d_2^* k^* \exp(-k^*) = cp^* k^{*2} \mp 1, \quad (67)$$

$$\begin{aligned} & 2c_1^* k^* \sinh k^* + 2c_3^* k^* \cosh k^* + 2c_1^* k^* \sinh k^* + 2c_3^* \sinh k^* \\ & + 2c_3^* \sinh k^* - \mu^* d_2^* k^* \exp(-k^*) - \mu^* d_4^* k^* \exp(-k^*) \\ & - 2\mu^* d_4^* \exp(-k^*) = \left[s^* \coth k^* - k^* \left\{ \frac{\kappa^*}{1 + \beta^* \lambda_d^*} + \frac{\mu_s^*}{1 + \beta^* \lambda_s^*} \right\} \right] \\ & \times [2c_1^* k^* \cosh k^* + 2c_3^* k^* \sinh k^* + 2c_3^* \cosh k^*], \quad (68) \end{aligned}$$

$$2c_1^* \sinh k^* + 2c_3^* \cosh k^* = (d_2^* + d_4^*) \exp(-k^*), \quad (69)$$

and

$$\begin{aligned} & 2c_1^* \cosh k^* + 2c_3^* \sinh k^* + 2\frac{c_3^*}{k^*} \cosh k^* \\ & = - \left(d_2^* + d_4^* - \frac{d_4^*}{k^*} \right) \exp(-k^*). \quad (70) \end{aligned}$$

The solution of Eqs. (67)–(70) for the dimensionless coefficients c_1^* , c_3^* , d_2^* and d_4^* would enable the evaluation of the dimensionless growth coefficient as given by

$$\beta^* = 2(c_1^* \sinh k^* + c_3^* \cosh k^*). \quad (71)$$

3. Results

The dimensionless parameters as defined by Eqs. (63)–(67) are specified. Equations (67)–(70) were numerically solved for the dimensionless coefficients c_1^* , c_3^* , d_2^* and d_4^* for different dimensionless wavenumbers and dimensionless growth coefficient was determined from Eq. (71). Typical plot of β^* vs k^* for different values of cp^* is shown in Fig. 2a. From Eq. (64), it can be seen that cp^* is inversely proportional to Hamaker constant and increases with film thickness. The film is found to be unstable for small wavenumbers as indicated by positive growth coefficient. There is a critical wavenumber k_c above which the film is stable and is given by, $k_c = (\Pi'(h)/\sigma)^{1/2}$. There is a dominant wavenumber k_m at which the growth coefficient is maximum. The maximum growth coefficient is higher for smaller values of cp^* . In other words, the film is more unstable for smaller film thickness and larger values of Hamaker constant. The maximum growth coefficient decreases with cp^* as shown in Fig. 2b. The effect of dimensionless dilatational (shear) relaxation times on maximum dimensionless growth coefficient for different values of dimensionless shear (dilatational) viscosities is shown in Fig. 3. The film is less stable (larger growth coefficient) for larger values of relaxation times. Also, the growth coefficient reaches asymptotic values for very large and very small relaxation times. The asymptotic value is independent of interfacial dilatational (shear) viscosity for large relaxation times. However, the asymptotic value for very small relaxation times is a function of interfacial dilatational (shear) viscosity and is smaller for larger values of the latter. As can be seen from Fig. 4, the maximum growth coefficient is larger (film less stable) for smaller values of dimensionless dilatational (shear) interfacial viscosities. Interestingly, the asymptotic values of the growth coefficient for very large and very small interfacial dilatational (shear) viscosities are independent of the relaxation times. The asymptotic values for very small and very large interfacial dilatational (shear) viscosi-

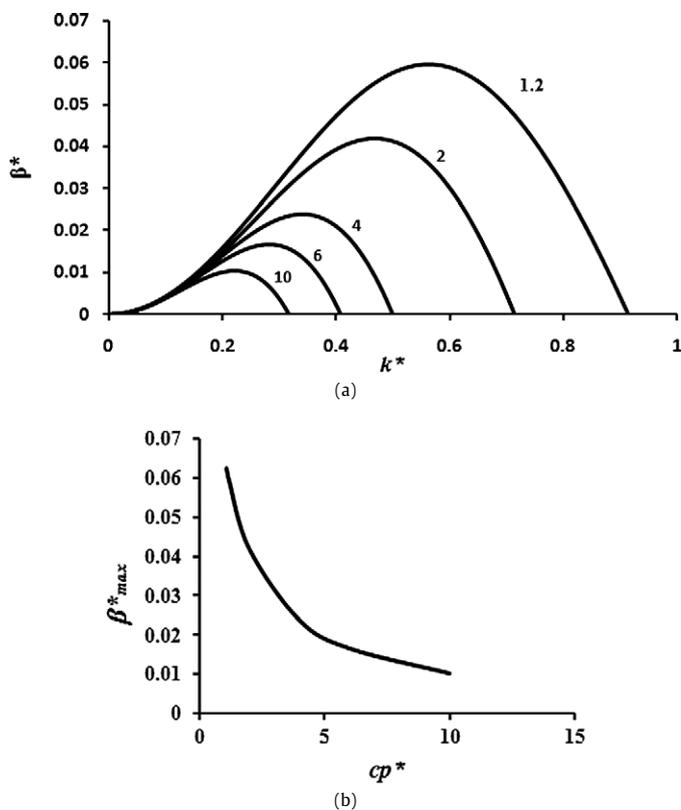


Fig. 2. (a) Plot of dimensionless growth coefficient versus dimensionless wavenumber for different values of cp^* . (b) Dimensionless maximum growth coefficient versus cp^* . Other parameter values are: $\mu^* = 1$, $s^* = -10$, $\lambda_d^* = 1$, $\lambda_s^* = 1$, $\kappa^* = 0.1$, $\mu_s^* = 0.1$.

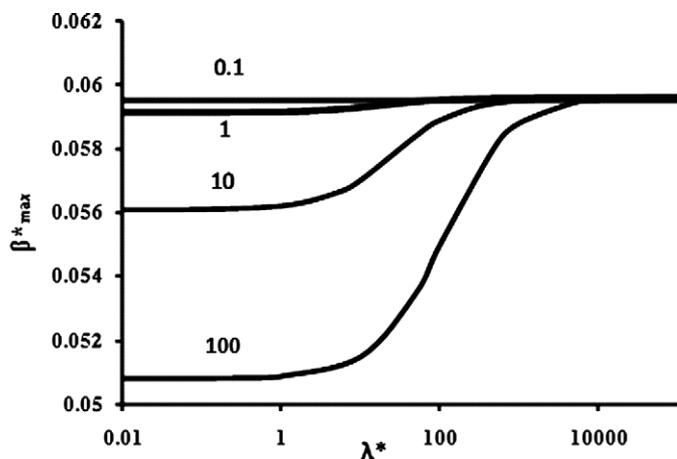


Fig. 3. Plot of dimensionless maximum growth coefficient versus λ_d^* (λ_s^*) for different values of κ^* (μ_s^*). Other parameter values are: $\mu^* = 1$, $s^* = -10$, $cp^* = 1.2$.

ties correspond to the values of growth coefficient for fully mobile and immobile interfaces respectively. The effect of viscosity ratio μ^* on maximum dimensionless growth coefficient is shown in Fig. 5 for different values of cp^* . As expected, the film is more stable (smaller growth coefficient) for larger viscosity ratios. Interestingly, the asymptotic value for very large viscosity ratio goes to zero and is independent of cp^* . However, the asymptotic value of growth coefficient for very small viscosity ratio is a strong function of cp^* and decreases for larger values of cp^* . Also, these asymptotic values for very small viscosity ratio refer to aqueous foam films.

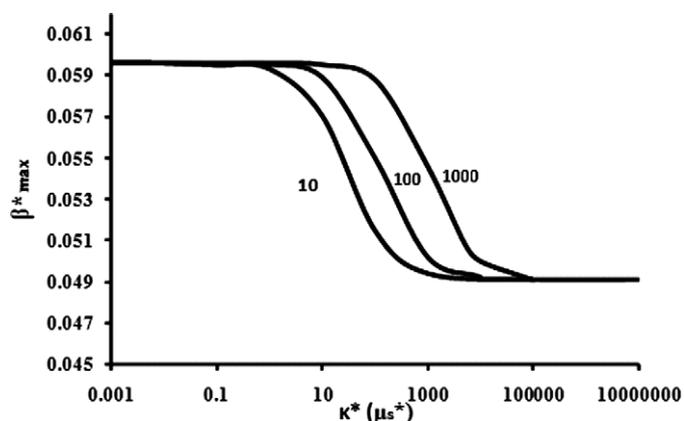


Fig. 4. Plot of dimensionless maximum growth coefficient versus κ^* (μ_s^*) for different values of λ_d^* (λ_s^*). Other parameter values are: $\mu^* = 1$, $s^* = -10$, $cp^* = 1.2$.

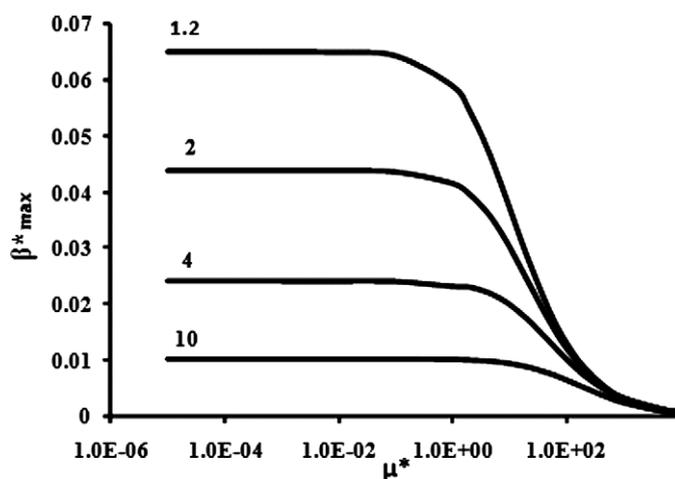


Fig. 5. Plot of dimensionless maximum growth coefficient versus μ^* for different values of cp^* . Other parameter values are: $\lambda_d^* = 0.1$, $\lambda_s^* = 0.1$, $s^* = -10$, $\kappa^* = 0.1$, $\mu_s^* = 0.1$.

The rupture time t_{rup} of an unstable film of thickness $2h$ is given by

$$\ln\left(\frac{h}{f_0}\right) = \beta^* \tau t_{rup}, \tag{72}$$

where f_0 is the amplitude of fluctuations. For thermal perturbations, the amplitude of initial perturbation can be taken as [10,31],

$$\begin{aligned} f_0 &= \left(\frac{2kT}{L}\right)^{1/2} (\Pi'(h) - \sigma k_m^2)^{-1/2} \\ &= \left(\frac{2kT}{\sigma}\right)^{1/2} \left(\frac{h}{L}\right)^{1/2} (k_c^2 - k_m^2)^{-1/2}. \end{aligned} \tag{73}$$

From Eqs. (71)–(72), one can evaluate the rupture time of a thin film.

4. Conclusions

Linear stability analysis for an aqueous film sandwiched between two oil phases with a viscoelastic oil–water interface is presented. The interfacial dilatational and shear viscoelastic properties were described by a Maxwell model. Perturbation growth coefficient is calculated in terms of film thickness and interfacial rheological properties. The maximum growth coefficient was found to decrease for smaller Hamaker constants and larger aqueous film thickness. The aqueous film is found to be more stable

for smaller values of dilatational (shear) relaxation times corresponding to interfacial rheological property and reaches asymptotic values for very large and small relaxation times. The maximum growth coefficient of aqueous film was larger (film less stable) for smaller values of interfacial dilatational (shear) viscosities. Also, the asymptotic values of maximum growth coefficient for very large and very small values of interfacial dilatational (shear) viscosities were found to be independent of relaxation times and correspond to those for immobile and fully mobile oil–water interfaces respectively. The aqueous film is shown to be more stable for larger viscosities of the oil phase with the maximum growth coefficient approaching zero as the ratio of viscosities of oil and aqueous phases approach very large values. The asymptotic values of maximum growth coefficient for very small viscosity ratios refer to those of aqueous foam films.

References

- [1] A. Vrij, F.T. Hesselink, J. Lucassen, M. van den Temple, *Proc. K. Ned. Akad. Wet. Ser. B* 73 (1970) 124.
- [2] E. Ruckenstein, R. Jain, *J. C. S. Faraday II* 70 (1974) 132.
- [3] R. Jain, E. Ruckenstein, *J. Colloid Interface Sci.* 54 (1976) 108–116.
- [4] E. Ruckenstein, C.S. Dunn, *Thin Solid Films* 51 (1978) 43.
- [5] A. Sharma, E. Ruckenstein, *Am. J. Optom. Physiol. Opt.* 62 (1985) 246.
- [6] C. Malderelli, R. Jain, in: I.B. Ivanov (Ed.), *Thin Liquid Films: Fundamentals and Applications*, vol. 29, Dekker, 1988, pp. 497–568.
- [7] A. Sharma, K. Kargupta, *Appl. Phys. Lett.* 83 (2003) 3549–3551.
- [8] L.Y. Yeo, O.K. Matar, *J. Colloid Interface Sci.* 261 (2003) 575–579.
- [9] A. Scheludko, *Adv. Colloid Interface Sci.* 1 (1967) 391–464.
- [10] G. Narsimhan, *J. Colloid Interface Sci.* 287 (2005) 624–633.
- [11] G. Narsimhan, Z. Wang, *J. Colloid Interface Sci.* 298 (2006) 491–496.
- [12] G. Narsimhan, Z. Wang, *Colloids Surf. A Physicochem. Eng. Aspects* 282 (2006) 24–36.
- [13] I.B. Ivanov, *Thin Liquid Films: Fundamentals and Applications*, Marcel Dekker, New York and Basel, 1988.
- [14] A. Sharma, J. Mittal, *Phys. Rev. Lett.* 89 (2002) 186101.
- [15] A. Sharma, *J. Colloid Interface Sci.* 199 (1998) 212–214.
- [16] A. Sathyagal, G. Narsimhan, *Chem. Eng. Commun.* 111 (1992) 161–175.
- [17] Y.L. Zhang, O.K. Matar, R.V. Craster, *J. Colloid Interface Sci.* 262 (2003) 130–148.
- [18] S.A. Safran, J. Klein, *J. Phys. II France* 3 (1993) 749–757.
- [19] G. Tomar, V. Shankar, S.K. Shukla, A. Sharma, G. Biswas, *Eur. Phys. J. E* 20 (2006) 185–200.
- [20] I.B. Ivanov, D.S. Dimitrov, *J. Colloid Polym. Sci.* 252 (1974) 982–990.
- [21] Z. Wang, G. Narsimhan, *Langmuir* 23 (2007) 2437–2443.
- [22] B.S. Murray, E. Dickinson, *Food Sci. Technol. Int.* 2 (1996) 131–145.
- [23] E.H. Lucassen-Reynders, *Food Struct.* 12 (1993) 1–12.
- [24] E. Dickinson, *Colloids Surf. B Biointerfaces* 20 (2001) 197–210.
- [25] S. Roth, B.S. Murray, E. Dickinson, *J. Agric. Food Chem.* 48 (2000) 1491–1497.
- [26] M.A. Bos, T. van Vliet, *Adv. Colloid Interface Sci.* 91 (2001) 437–471.
- [27] Z. Wang, G. Narsimhan, *Langmuir* 21 (2005) 4482–4489.
- [28] G. Narsimhan, Z. Wang, *J. Colloid Interface Sci.* 291 (2005) 296–302.
- [29] D.S. Valkovska, K.D. Danov, I.B. Ivanov, *Colloids Surf. A Physicochem. Eng. Aspects* 175 (2000) 179–192.
- [30] D.A. Edwards, H. Brenner, D.T. Wasan, *Interfacial Transport Processes and Rheology*, Butterworth–Heinemann, Boston, 1991.
- [31] J.G.H. Joosten, in: I.B. Ivanov (Ed.), *Thin Liquid Films: Fundamentals and Applications*, vol. 29, Marcel Dekker, New York and Basel, 1988, pp. 569–662.